

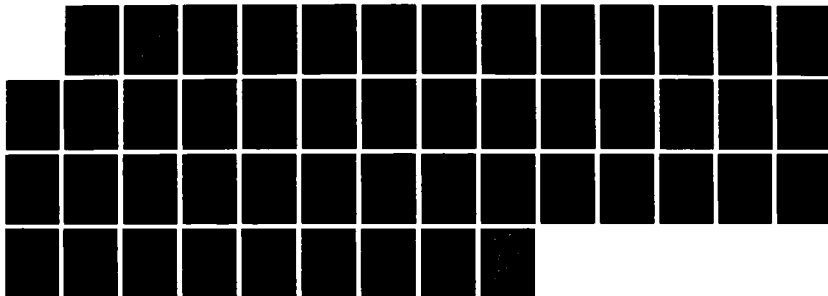
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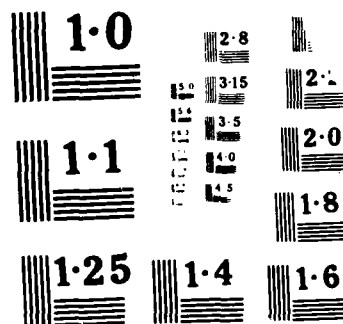
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Report C86-12

**COMPACT REGENERABLE SULFUR SCRUBBER FOR  
PHOSPHORIC ACID FUEL CELLS**

Prepared by:

José Giner, Ph.D.  
Cecelia C. Cropley

GINER, INC.  
14 Spring Street  
Waltham, MA 02254-9147

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November, 1987

Final Report

September 30, 1986 - September 30, 1987

Contract No. DAAK70-86-C-0113

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## EXECUTIVE SUMMARY

Under a one-year reduced level of effort Phase II SBIR contract with the U.S. Army Belvoir RD&E Center, Giner, Inc. has conducted an investigation for the desulfurization of unprocessed (non-reformed) diesel fuel for use in modular phosphoric acid fuel cell (PAFC) generators.

Incorporation of the technology for desulfurization of unprocessed diesel fuel into a PAFC power plant may decrease the size and weight of the fuel processing system. An alternative to current PAFC fuel processing technology may be a pre-reformer sorbent bed, using the technology for desulfurization of unprocessed diesel, followed by a post-reformer regenerable sorbent bed to remove the remaining  $H_2S$ . Replacing the currently used high pressure, bulky hydrodesulfurization unit with an atmospheric pressure desulfurizer of current technology (developed in this program) should reduce the weight and volume of the sulfur removal unit by a minimum of 25%.

The effort in this program concentrated on developing a regenerable mixed metal oxide sorbent for the desulfurization of diesel fuel. The emphasis was on the development of a regenerable sorbent with a high sulfur capacity.

Fourteen sorbents were evaluated, all containing a mixture of copper oxide and iron, manganese, or zinc oxides. Both unsupported oxides and oxides of varying metal ratios supported on zeolite or alumina were evaluated. Of the sorbents tested, the three best appear to be: zeolite-supported  $CuO/Fe_xO_y$  with a 2.7 Fe:Cu atomic ratio; zeolite-supported  $CuO/MnO$ ; and alumina-supported  $CuO/Fe_xO_y$ . These sorbents had the highest sulfur loadings, approximately 1 wt%, which corresponds to a theoretical conversion of metal oxides to sulfides of approximately 20%.

In this program, the removal of greater than 60% of the sulfur from unprocessed diesel was demonstrated. Preliminary studies also

indicated that the sorbents are regenerable, with up to 70% of the sorbed sulfur removed during regeneration.

The mechanism of direct desulfurization of diesel was also briefly investigated. The mechanism is complex and not completely understood, but partial cracking of the diesel occurs, as well as direct sorption of some of the large organic sulfur compounds. Cracking of the diesel is more severe on zeolite-supported sorbents than on other sorbents tested.

Improvement in sorbent sulfur loading, sulfur removal efficiency and sorbent regenerability are expected with optimization of sorbent composition, sorbent structure and operating conditions.



### ACKNOWLEDGEMENTS

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Those who contributed to this study were Dr. A.B. LaConti, Dr. J.A. Kosek, Mr. Clyde Brooks, Ms. Lynne McConchie, and Mr. Steven Melly of Giner, Inc. We would also like to thank Dr. Maria Flytzani-Stephanopoulos of the Massachusetts Institute of Technology for providing sorbent samples and technical advice.

## TABLE OF CONTENTS

REPORT DOCUMENTATION PAGE .....	i
EXECUTIVE SUMMARY .....	ii
ACKNOWLEDGEMENTS .....	iv
TABLE OF CONTENTS .....	v
LIST OF FIGURES .....	vi
LIST OF TABLES .....	vi
1.0 INTRODUCTION .....	1
2.0 EXPERIMENTAL PROCEDURES .....	4
2.1 Desulfurization .....	4
2.2 Regeneration .....	7
2.3 Analytical Methods .....	8
2.4 Sorbent Preparation .....	9
3.0 RESULTS .....	12
3.1 Sorbent Sulfur Capacity Studies .....	12
3.2 Regeneration Studies .....	17
3.3 Sulfur Concentration in Effluent Diesel .....	21
3.4 Effect of Operating Conditions on Sorbent Sulfur Loadings .....	23
3.4.1 Temperature .....	23
3.4.2 Carrier Gas Composition .....	25
3.4.3 Space Velocity .....	25
3.4.4 Sorbent Pre-Reduction .....	26
3.5 Mechanism of Desulfurization .....	28
4.0 CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK .....	35
4.1 Conclusions .....	35
4.2 Future Work .....	36
5.0 REFERENCES .....	37

## LIST OF FIGURES

FIGURE 1	Block Diagram of a Conventional PAFC Fuel Processing Train .....	1
FIGURE 2	Desulfurization Test Unit .....	5
FIGURE 3	Chromatogram of Unprocessed Diesel .....	29
FIGURE 4	Peak Areas vs. Retention Time for Several Sorbents .....	30
FIGURE 5	Peak Areas vs. Retention Time for Unsupported Sorbents .....	31
FIGURE 6	Peak Areas vs. Retention Time for Zeolite-Supported Sorbents .....	33
FIGURE 7	Peak Areas vs. Retention Time at Various Times During a Desulfurization Run .....	34

## LIST OF TABLES

TABLE 1	Standard Operating Conditions for Sorbent Screening Tests .....	6
TABLE 2	Range of Operating Conditions Utilized .....	6
TABLE 3	Source and Composition of Sorbents Tested .....	11
TABLE 4	Sorbent Sulfur Loadings .....	13
TABLE 5	Effect of Cu/M Ratio on Sorbent S Loading .....	15
TABLE 6	Theoretical Sulfur Capacity and Percent of Theoretical Attained for Selected Sorbents .....	17
TABLE 7	Sulfur Content of Regenerated Sorbents .....	18
TABLE 8	Effect of Saturator Temperature and Duration of Oxidation Step on Sorbent Regenerability Over Two Cycles .....	19
TABLE 9	2.7 Fe:Cu CuO/Fe <sub>x</sub> O <sub>y</sub> Surface Area and Sulfur Content in Fresh, Sulfided, and Regenerated States .....	20
TABLE 10	Sulfur Concentration in Effluent Diesel .....	22
TABLE 11	Effect of Temperature on Sulfur Loading and Carbon Content of the G66B Sorbent .....	24
TABLE 12	Average Sorbent Sulfur Loadings at 400°C and 500°C ...	24
TABLE 13	Effect of Carrier Gas Composition on Sorbent Sulfur Loadings .....	25
TABLE 14	Effect of Pre-Reduction on Sorbent Sulfur Loadings ...	27

## 1.0 INTRODUCTION

Under a one-year reduced level of effort, Phase II SBIR contract with the US Army Belvoir RD&E Center, Giner, Inc. investigated a regenerable sulfur scrubbing process for use in modular phosphoric acid fuel cell (PAFC) generators.

The overall objective of this program was to develop a lightweight, compact, cost-effective method of desulfurizing diesel fuel to supply a PAFC with fuel gas hydrogen containing <10 ppm sulfur. At the time the program was conceived, the Army was interested in developing modular, transportable PAFC generators that would use logistic fuels, primarily diesel, as a source of hydrogen. An important consideration in the design of these generators was the overall weight and volume of the units. The fuel cell itself can be made lightweight and compact, but a fuel processing train for the conversion of diesel to sulfur free, low CO content hydrogen adds excessive weight and volume.

A schematic block diagram for the fuel processing section of a diesel fueled phosphoric acid fuel cell is shown below:

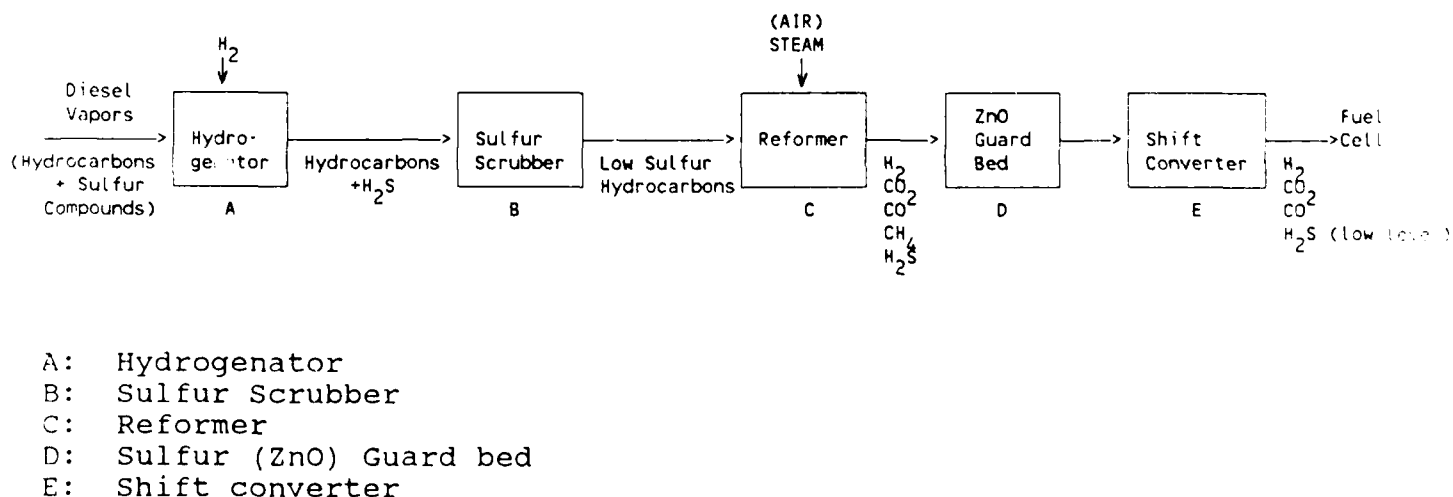


Figure 1 Block Diagram of a Conventional PAFC Fuel Processing Train

These five units perform **three** basic functions:

- **Bulk Sulfur Removal:** Unit A, hydrogenation step of hydrodesulfurization (HDS), converts organic sulfur to  $H_2S$ ; it requires hydrogen gas feed. Unit B (Bulk Sulfur Scrubber) reduces the sulfur (now as  $H_2S$ ) content of diesel fuel to levels which can be tolerated by a conventional reformer (Unit C), (typically less than 200 ppm  $H_2S$ ).

- **Steam Reforming:** Unit C converts the now low sulfur hydrocarbon fuel to  $H_2$ ,  $CO_2$  and CO. Small amounts of  $H_2S$  still remain. The carbon monoxide level in the post reformer stream is about 10-20% and must be reduced to below 1%.

Unit C is assumed to be a conventional steam reformer using a nickel based catalyst. Nickel based catalysts are very sulfur sensitive, but are more efficient than catalysts which are more sulfur tolerant.

- **Reduction of CO Content:** Unit E shifts water and carbon monoxide to hydrogen and carbon dioxide. The shift conversion reaction is favored at relatively low temperatures ( $175^{\circ}C$  -  $350^{\circ}C$ ) where the shift conversion catalyst is very sulfur sensitive. A ZnO guard bed, Unit D, is required to lower the  $H_2S$  content of the shift converter feed to acceptable levels for PAFC fuels (typically less than 10 ppm  $H_2S$ ).

The three units required for sulfur removal contribute significantly to the weight and volume, as well as the complexity, of the power plant. For a modular 150 kw power plant, the weight of the HDS unit (including the sulfur scrubber) is approximately 15% of the total system weight (1).

With the goal of reducing the weight and volume of the fuel processing train, the effort in this program concentrated on developing technology for the regenerable direct desulfurization of unprocessed (non-reformed) diesel fuel on mixed metal oxide

sorbents. This technology was aimed at replacing the HDS unit, including the sulfur scrubber, and the final ZnO guard bed in a conventional fuel cell power plant with a single pre-reformer regenerable sulfur removal unit. A regenerable sorbent bed prior to the reformer would provide a lightweight and compact method of sulfur removal, while allowing the more efficient sulfur intolerant reformers to be used, and eliminating the final sulfur guard bed.

The effort to develop this technology grew out of the work conducted in Phase I of this program. In the Phase I program, under Contract No. DAAK70-85-C-0096 with the US Army Belvoir R&E Center, the feasibility of a regenerable, high-temperature sorption process for removing sulfur from reformed diesel fuel was established (2). For a simulated reformed diesel fuel, the sulfur concentration, as  $H_2S$ , was reduced from 100 ppm in the feed to less than 10 ppm in the reactor effluent. The CuO/ZnO sorbent used in this study showed excellent regenerability. Replacing the throw-away ZnO guard bed in a conventional fuel processing train with a post-reformer regenerable sorbent bed could result in considerable savings in weight and volume. With this configuration, however, a sulfur removal step before the reformer, or the use of a less-efficient, sulfur-tolerant, reforming catalyst would be required. A preferred option is the removal of sulfur from diesel fuel before the reformer. This would provide greater savings in weight and volume of the fuel processing train, as well as simplify the process. However, desulfurization of unprocessed diesel is difficult because the sorbent must remove large organic sulfur compounds, rather than  $H_2S$ . In the Phase I program, preliminary studies indicated greater than 40% removal of sulfur by sorption on mixed metal oxides. These results were promising enough to focus the Phase II effort on development of this technology.

The major objective of the reduced scope Phase II program was to develop the technology for desulfurization of unprocessed diesel using copper based mixed metal oxide sorbents. The emphasis was on the development of a regenerable sorbent with a high sulfur capacity. Some effort was also devoted to investigating the

effects of temperature, carrier gas composition and space velocity on sorbent sulfur removal efficiency and capacity. A preliminary investigation of the mechanism of desulfurization on the various sorbents was also conducted.

## 2.0 EXPERIMENTAL PROCEDURES

The desulfurization and regeneration studies were conducted in a fixed bed, atmospheric pressure reactor, shown in Figure 2. The reactor consisted of a stainless steel tube lined with a 1.6 cm ID quartz tube, packed with 5-10 grams of sorbent, forming a sorbent bed approximately 4 cm in length. Both below the sorbent bed, for support, and above the bed, for flow distribution, the reactor was packed with porcelain saddles. A thermocouple was located in the center of the sorbent bed. The reactor was heated with a Hoskins tube furnace.

The diesel fuel used in this program was purchased from a local service station. The quantity of diesel purchased was sufficient to last the entire length of the program. It contained 1340 ppmw sulfur. All of the gases ( $N_2$ ,  $H_2$ , air) used in this program were supplied from cylinders, with their flow regulated by metering valves and measured by rotameters.

### 2.1 Desulfurization

During desulfurization runs, diesel flowed through electrically heated lines to a junction slightly before the reactor entrance, where the vaporized diesel was mixed with heated carrier gas. The mixture then flowed down through the reactor to the sorbent bed where desulfurization occurred. The reactor effluent was run through a water-cooled condenser and into a collection flask; the non-condensable gases were vented. The concentration of  $H_2S$  in the non-condensable gases was periodically measured with Sensidyne or Kitagawa gas detection tubes. At the end of the run, the reactor was dismantled, and a portion of the sorbent analyzed





for total sulfur content. The sulfur content of selected condensed diesel samples was also analyzed.

The standard operating conditions during the sorbent screening tests are listed in Table 1. These conditions were selected after a preliminary investigation of the effect of operating conditions on sulfur removal, discussed in Section 3.4. These conditions were used for the bulk of the testing; the range of operating conditions utilized in this program is listed in Table 2.

**TABLE 1**

**Standard Operating Conditions for  
Sorbent Screening Tests**

Temperature:	500°C
Carrier Gas:	H <sub>2</sub> at 100 cc/min
Diesel Flow Rate:	0.5 cc/min
Diesel Liquid Space Velocity:	4.3 hr <sup>-1</sup>
Duration of Run:	4 hours

Sorbent fresh and not reduced prior to the run.

**TABLE 2**

**Range of Operating Conditions Utilized**

Temperature:	400°, 500°, 650°C
Carrier Gas:	H <sub>2</sub> , N <sub>2</sub> , H <sub>2</sub> /H <sub>2</sub> O (approx. 50/50)
Diesel Flow Rate:	0.14 cc/min, 0.5 cc/min
Diesel Liquid Space Velocity:	0.5 hr <sup>-1</sup> , 4.3 hr <sup>-1</sup>
Duration of Run:	2 hours, 4 hours

Both pre-reduced and non pre-reduced sorbents were tested.

During the course of the project, revisions to the diesel flow system were made. Initially, a variable flow, plunger-type metering pump was used. However, the pump was oversized for the typical diesel flow of 0.5 cc/min. To produce this low flow, the pump took about two strokes/minute. At this setting, the flow rate

appeared to vary slightly, and frequent calibration was required. Also, due to the pulsing operation of the pump, a rotameter could not be used.

Approximately six months into the program, the metering pump was replaced with a pressurized flow system. In this system, a constant  $N_2$  pressure forced diesel out of a tank, through a metering valve and rotameter, to the reactor. With this pressurized system, the diesel flow was constant, measurable, and reproducible, and required only initial calibration of the rotameter.

Several desulfurization tests used a carrier gas containing approximately 50% water to evaluate the effect of water on sorbent sulfur loading and fuel cracking. In these experiments, the carrier gas was bubbled through a saturator which contained water at a known and constant temperature. This saturator was also used to humidify the regeneration air stream.

Reduction of the sorbent prior to desulfurization was also evaluated in a few runs. Two different pre-reduction procedures were used. Initially the sorbent was pre-reduced overnight with a low concentration of  $H_2$  (approximately 2%) in  $N_2$  at a bed temperature of  $250^\circ C$ . Later the pre-reduction step was accelerated, running 50%  $H_2$  in  $N_2$  through the reactor for one hour, with the sorbent bed at  $500^\circ C$ .

## 2.2 Regeneration

Several different regeneration conditions were evaluated during the course of the program. Basically, however, the sorbent was regenerated upflow at a sorbent bed temperature of  $650-750^\circ C$  using a water/air stream for 1 to 2 hours, followed by an overnight purge with  $N_2$  at a bed temperature of  $700-800^\circ C$  to decompose metal sulfates. Two different compositions of the regeneration gas stream were tested: 50% water/50% air and 80% water/20% air. The water content was varied by changing the saturator temperature.

The regeneration effluent gases were passed through a scrubber to absorb the  $\text{SO}_2$  produced during regeneration. From the amount of  $\text{SO}_2$  absorbed, a semi-quantitative measure of the extent of regeneration was obtained. During the initial regeneration runs, a sodium hydroxide solution was used in the scrubber; the amount of  $\text{SO}_2$  absorbed was determined by titrations of the hydroxide with hydrochloric acid. However, the calculations based on sodium hydroxide usage indicated that sorbent regeneration was complete, while actual analysis of the regenerated sorbents showed that sulfur was still present. It appears that some other component of the regeneration effluent stream, probably  $\text{CO}_2$ , also neutralized the hydroxide. When this was discovered, the sodium hydroxide was replaced by an iodine solution which was titrated with sodium thiosulfate. The qualitative values for extent of regeneration obtained from the iodine absorption method were in good agreement with the sorbent sulfur analysis.

### 2.3 Analytical Methods

The routine analyses performed in this program consisted of total sulfur analysis of the sulfided or regenerated sorbent, and concentration of  $\text{H}_2\text{S}$  in the non-condensable reactor effluent gases. Selected samples of condensed diesel were analyzed for total sulfur content. During the last three months of the program, a gas chromatograph was used to qualitatively identify the changes occurring to the diesel sulfur compounds throughout the course of a desulfurization run.

The total sulfur analyses of the condensed diesel and sulfided/regenerated sorbents was performed by an outside laboratory, Luvak, Inc. in Boylston, MA. To confirm Luvak's results, samples were occasionally sent to a second laboratory, Galbraith Laboratories, Inc. in Knoxville, TN.

The concentration of  $\text{H}_2\text{S}$  in the non-condensable reactor effluent gas was monitored at approximately thirty (30) minute

intervals throughout a desulfurization run using Sensidyne or Kitagawa gas detection tubes. The lower detection limit of  $H_2S$  with the tubes is 2-3 ppm. During the first few runs of this program, attempts to measure the COS and  $CS_2$  concentration in the reactor effluent with gas detection tubes were made, but interference by hydrocarbon vapors prevented accurate measurements.

The sulfur species in diesel fuel were analyzed with a Varian 3400 gas chromatograph equipped with a sulfur sensitive flame photometric detector (FPD). A 6' x 1/8" stainless steel column packed with 3% SP-2100 on 80/100 mesh Supelcoport obtained from Supelco, Inc. was used to separate the diesel components. For analysis of diesel samples, the GC method was: injection port temperature of 350°C;  $N_2$  carrier gas at 30 ml/min; initial column temperature of 60°C, held for three minutes; temperature ramp to 300°C at 8°C/min.

Since there are more than 20 sulfur containing species in diesel fuel, many of which are unidentified, the diesel chromatograms were used to determine shifts in relative peak sizes due to the desulfurization reaction, rather than to quantitatively determine the concentration of a particular sulfur species or the total sulfur concentration. For comparing chromatograms from various runs, the areas of selected peaks were normalized by dividing the peak area by the average area of the corresponding peaks in fresh diesel.

In addition to the routine analyses, the structural and chemical properties of selected sorbents were evaluated using BET surface area, X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses. These analyses were all performed by outside laboratories.

#### **2.4 Sorbent Preparation**

Nine of the fourteen mixed metal oxide sorbents tested in this program were prepared by Giner, Inc. All of the sorbents

prepared by Giner, Inc. were supported on commercially available materials: Linde SK-500 faujasite  $\gamma$  zeolite, Harshaw alumina Al-4126 or United Catalysts alumina T-2432. The unsupported sorbents were either obtained commercially (United Catalysts G66B) or were provided by Dr. M. Stephanopoulos of the Massachusetts Institute of Technology (MIT). The sorbents obtained from Dr. Stephanopoulos are in a highly dispersed, porous form prepared by a gelation technique (3). The sources and compositions of all of the sorbents tested are listed in Table 3.

The supported sorbents were prepared by impregnation of the appropriate metal nitrate salts in aqueous solution on the support, which had been pre-stabilized by heat treatment at 700°C (500°C for T-2432 alumina). The concentrations of the metal nitrate solutions were chosen to produce a total metal loading of approximately 10 wt%. After impregnation, the sorbent was dried overnight at 105-110°C, and then heat-treated in a horizontal tube furnace in air for approximately 3 hours. The heat treatment temperature was 700°C, except for the  $\text{CuO}/\text{Fe}_x\text{O}_y$  supported on United Catalysts T-2432 alumina, which was heat-treated at 500°C to minimize the formation of copper aluminates. Following the heat treatment, the metal loading of the sorbents was analyzed by Galbraith Laboratories, Inc.

The oxidation states of the iron and manganese oxides following the heat treatment step are most likely to be  $\text{Fe}_2\text{O}_3$  and  $\text{MnO}$ , respectively, although this could not be confirmed analytically due to the low metal loadings. However, in the reducing atmosphere of the desulfurizer, the oxidation state of the iron oxides may change, possibly producing mixed oxidation states. Due to this uncertainty, the iron oxides in the sorbents prepared at Giner, Inc. are referred to as  $\text{Fe}_x\text{O}_y$  throughout this report.

TABLE 3

## Source and Composition of Sorbents Tested

Supported Sorbents Prepared By Giner, Inc.				
Type	wt% Cu	wt% Other Metal	Atomic Ratio (Cu/M)	Support
CuO/ZnO 1.1 Cu:Zn	4.15	3.89	1.1/1	faujasite y SK-500 zeolite
CuO/MnO <sub>x</sub>	5.37	5.44	1/1.2	"
CuO/Fe <sub>x</sub> O <sub>y</sub>	3.75	3.78	0.9/1	"
CuO/ZnO 2Cu:Zn	5.21	2.61	2.05/1	"
CuO/Fe <sub>x</sub> O <sub>y</sub> 1.3 Cu:Fe	4.50	3.02	1.3/1	"
CuO/Fe <sub>x</sub> O <sub>y</sub> 1.5 Cu:Fe	5.52	3.20	1.5/1	"
CuO/Fe <sub>x</sub> O <sub>y</sub> 2.7 Fe:Cu	2.11	4.97	1/2.7	"
CuO/Fe <sub>x</sub> O <sub>y</sub>	3.75	3.87	1/1.2	alumina Harshaw Al-4126
CuO/Fe <sub>x</sub> O <sub>y</sub>	4.79	4.02	1.05/1	alumina United Catalysts T-2432

Unsupported Sorbents		
Type	Composition	Source
CuO/ZnO G66B	65% ZnO, 33% CuO, 2% Al <sub>2</sub> O <sub>3</sub>	United Catalysts
CuO/Fe <sub>2</sub> O <sub>3</sub>	Assume ferrite composition	MIT
3CuO/Fe <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	Approximately 48% CuO, 32% Fe <sub>2</sub> O <sub>3</sub> , 20% Al <sub>2</sub> O <sub>3</sub>	MIT
CuO/Al <sub>2</sub> O <sub>3</sub>	50% CuO, 50% Al <sub>2</sub> O <sub>3</sub>	MIT
3CuO/2ZnO	Approximately 60% CuO, 40% ZnO	MIT

### 3.0 RESULTS

Most of the effort in this program was concentrated on determining the sulfur loading capacities of the sorbents under consideration. Some effort was also devoted to sorbent regeneration studies and investigations of the effects of temperature, carrier gas composition and space velocity on sorbent sulfur removal efficiency and capacity. A preliminary investigation of the mechanism of desulfurization on the various sorbents was also conducted.

#### 3.1 Sorbent Sulfur Capacity Studies

Fourteen copper based mixed metal oxide sorbents, both supported and unsupported, were evaluated for sulfur loading capacity under standard conditions in a series of screening tests. In these studies the sorbent was analyzed for total sulfur content after a four-hour diesel desulfurization run at 500°C with H<sub>2</sub> as the carrier gas. The sorbent sulfur loadings ranged from 0.3 to 1.2 wt%, as shown in Table 4. The three sorbents with the consistently highest loadings, in the 0.9-1.0 wt% range were: zeolite-supported CuO/Fe<sub>x</sub>O<sub>y</sub> with a 2.7 Fe:Cu atomic ratio; zeolite-supported CuO/MnO; and alumina (Harshaw Al-4126)-supported CuO/Fe<sub>x</sub>O<sub>y</sub>. Although there was considerable scatter in the sulfur loading data, these three sorbents appear to have significantly higher loadings than the other sorbents, with the possible exception of the unsupported 3CuO/Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> sorbent, for which the data was very mixed.

For the supported sorbents, the sulfur loadings were normalized on the basis of the sorbent molar metal content. The normalization accounts for differences in the sorbent metal loadings which may effect the sulfur loading capacity. Although normalizing the loadings changes the rank of the sorbents slightly, the three sorbents with the highest absolute sulfur loadings also have the highest normalized loadings. Due to the scatter in the data, and

TABLE 4

## Sorbent Sulfur Loadings

Sorbent	Range of Loadings (wt%)	Average Loading (wt%)	Normalized Avg. Loading (wt%)
CuO/Fe <sub>x</sub> O <sub>y</sub> 2.7Fe:Cu <sup>y</sup> zeolite	0.71-1.2	0.96	7.58
CuO/MnO zeolite	0.9-1.02	0.96	5.24
CuO/Fe <sub>x</sub> O <sub>y</sub> alumina (Al-4126)	0.66-0.97	0.81	6.30
3CuO/Fe <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub> unsupported	0.42-1.30	0.77	
CuO/ZnO G66B (United Catalysts) unsupported	0.45-0.613	0.56	
CuO/ZnO 1.1 Cu:Zn zeolite	0.34-0.77	0.56	4.45
CuO/Fe <sub>x</sub> O <sub>y</sub> 0.9Cu:Fe <sup>y</sup> zeolite	0.32-1.06	0.51	4.02
3CuO/2ZnO unsupported	0.43-0.52	0.48	
CuO/Fe <sub>x</sub> O <sub>y</sub> alumina (T-2432)	0.37-0.58	0.48	3.2
CuO/Al <sub>2</sub> O <sub>3</sub> unsupported	0.45	0.45	
CuO/Fe <sub>x</sub> O <sub>y</sub> 1.3Cu:Fe <sup>y</sup> zeolite	0.20-0.63	0.44	2.82
CuO/Fe <sub>x</sub> O <sub>y</sub> 1.5Cu:Fe <sup>y</sup> zeolite	0.41-0.42	0.42	2.9
CuO/ZnO 2Cu:Zn zeolite	0.27	0.27	2.22
CuO/Fe <sub>2</sub> O <sub>3</sub> unsupported	0.12-0.30	0.21	



the relatively small amount of data available, the differences in loadings between the top three sorbents are not significant.

Examination of the sulfur loading data indicates that for the supported sorbents, the ratio of metals may be more important than the type of metal present. As shown in Table 5, the sorbent sulfur loading decreases as the atomic ratio of copper to the other metal present in the sorbent increases. This trend holds for all three metals investigated, Fe, Mn, and Zn. However, this trend does not hold for the unsupported sorbents, where the highest sulfur loading was obtained on a sorbent with a high Cu to Fe ratio ( $3\text{CuO}/\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ ). The conflicting data is interesting but is difficult to explain without detailed mechanistic and physical studies. Further work is required to determine if the trend on the supported sorbents holds over a wider range of compositions, and if so, to explain it.

There was a considerable amount of scatter in the sulfur loading data, as indicated by the range of loadings for the various sorbents listed in Table 4. For two runs on the same sorbent under the same operating conditions, the sulfur loadings often varied by a factor of two. There are several possible causes of the scatter, including channeling of the bed, sorbent non-homogeneities, and the steep sulfur gradient in the bed. Due to the small size of the bed, its low length to diameter ratio ( $<3$ ), and the relatively large size of the sorbent pellets in comparison to the bed diameter, bed channeling is the most likely explanation for the scatter.

The 0.9-1.0 wt% sulfur loadings obtained in this program appear to be quite low when compared with the typical loadings of 10-15 wt% (4) on similar sorbents used in desulfurization of coal gas or reformed fuels. However, in that application the sorbents are primarily removing  $\text{H}_2\text{S}$ ,  $\text{COS}$ ,  $\text{CS}_2$  and other low molecular weight sulfur gases, compared to the complex high molecular weight sulfur compounds that must be removed when desulfurizing unprocessed

**TABLE 5**  
**Effect of Cu/M Ratio on Sorbent Sulfur Loading**

Supported Sorbents				
Cu/M Ratio	M	Support	S Loading	Normalized S Loading
0.37	Fe	Zeolite	.96	7.58
0.83	Mn	Zeolite	.96	5.24
0.83	Fe	Al-4126	.91	6.30
0.9	Fe	Zeolite	.51	4.02
1.05	Fe	T-2432	.48	3.22
1.1	Zn	Zeolite	.56	4.45
1.3	Fe	Zeolite	.44	2.80
1.5	Fe	Zeolite	.42	2.98
2.0	Zn	Zeolite	.27	2.22

Unsupported Sorbents			
Cu/M Ratio	M	Sorbent	S Loading
0.5	Fe	CuO/Fe <sub>2</sub> O <sub>3</sub>	0.12-.3
0.52	Zn	G66B	.56
1.5	Zn	3CuO/2ZnO	.48
1.5	Fe	3CuO/Fe <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	.77
	Cu only	CuO/Al <sub>2</sub> O <sub>3</sub>	.43

diesel. When removing H<sub>2</sub>S, the reaction on the sorbent is simply conversion of the metal oxide to metal sulfide with production of water. With aromatic or long chain high molecular weight sulfur species, however, the reaction mechanism is complex and not completely understood. Our research, discussed in Section 3.5, indicates that some cracking of the diesel occurs, forming lower molecular weight sulfur species. Direct sorption of both high and

low molecular weight sulfur compounds also occurs. These sulfur compounds may be quite large, too large to enter the internal sorbent pores, and therefore, would be adsorbed on the surface. With these large molecules on the sorbent surface, stearic hindrance would prevent other molecules from being adsorbed, leading to low utilization of the sorbent.

The utilization of the metal oxides in the zeolite-supported sorbents was actually not as low as initial indications suggest. Since the total metal loadings on the zeolite-supported sorbents are only approximately 10 wt%, the theoretical sulfur capacities, based on full conversion of the oxides to sulfides, is less than 5 wt%, as opposed to 38 wt% for the unsupported G66B. For the 2.7 Fe:Cu and CuO/MnO zeolite-supported sorbents, the 0.96 wt% sulfur loading attained in this program corresponds to approximately 20% of the theoretical sulfur capacity. This is a respectable conversion; a 10 wt% loading on pure zinc ferrite corresponds to a 25% theoretical conversion. Table 6 lists the loadings and conversions for selected sorbents.

However, the theoretical conversions attained on the unsupported sorbents tested in this program were very low. For the unsupported  $3\text{CuO}/\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$  sorbent, which had the highest sulfur loading among the unsupported sorbents, only 2.7% of theoretical conversion was attained. This low conversion may indicate that only the outer surface of the unsupported sorbent is utilized in direct sorption of large organic sulfur compounds.

Further improvement in sorbent sulfur loadings requires further optimization of the supported materials with respect to surface area, pore volume, metal loading, and other physical/chemical factors. It should be emphasized that it is not uncommon to have loadings in the 1-2 wt% range during the initial sorbent development stage.

TABLE 6

Theoretical Sulfur Capacity and Percent of Theoretical Attained for Selected Sorbents

Sorbent	S Loading (wt%)	Theoretical S Capacity (wt%)	% of Theoretical Attained
<b>SUPPORTED</b>			
CuO/MnO zeolite	0.96	4.52	21.2
2.7 Fe:Cu zeolite	0.96	4.79	20.0
CuO/Fe <sub>x</sub> O <sub>y</sub> Al-4126	0.81	4.24	19.1
<b>UNSUPPORTED</b>			
G66B CuO/ZnO	0.56	38.8	1.4
3CuO/Fe <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	0.77	28.8	2.7

### 3.2 Regeneration Studies

Preliminary investigations of sorbent regenerability were conducted. Five sorbents were run through two desulfurization/regeneration cycles to determine the extent of sorbent regenerability, which was obtained from an analysis of the sulfur content of the regenerated sorbent. As shown in Table 7, the lowest residual sulfur loading, 0.2 wt%, was obtained on the United Catalysts G66B CuO/ZnO sorbent. This low residual loading corresponds to a removal of over 60% of the sulfur sorbed during the desulfurization step. The residual sulfur loadings on the other sorbents tested were generally in the 0.4-0.7 wt% range.

TABLE 7

## Sulfur Content of Regenerated Sorbents

Sorbent	Run Nos.	Wt% Sulfur
CuO/Fe <sub>x</sub> O <sub>y</sub> 1.5 Cu:Fe zeolite	69/70	0.46
CuO/Fe <sub>x</sub> O <sub>y</sub> 2.7 Fe:Cu zeolite	76/77	0.70
	86/87	0.58
CuO/MnO	71	0.53
	72/73	0.90
	82/83	0.54
	98	0.38
CuO/ZnO zeolite	74/75	0.68
	88/89	0.58
CuO/ZnO G66B	80/81	0.28
	92/93	0.20

In the initial regeneration tests, the sorbent was regenerated for approximately 1 hour, at a sorbent bed temperature of 650°C-750°C with a gas composition of approximately 50% water/50% air. An overnight purge with N<sub>2</sub> at a sorbent bed temperature of 700°C-800°C was conducted to decompose metal sulfates which may have formed during the first regeneration step. At these operating conditions, the residual sulfur loadings were fairly high, generally above 0.6 wt%. To improve the regeneration, the water concentration in the gas stream was increased to approximately 80% by raising the saturator temperature, and the duration of the oxidation step was increased to 2 hours. As shown in Table 8, the residual sulfur content of the sorbents after two cycles decreased with the increase in duration and in the water content, except for the G66B sorbent. From the data it is difficult to determine whether the increase in water content or duration was more effective in improving the regenerability, since these factors were not studied individually.

TABLE 8

Effect of Saturator Temperature and Duration of Oxidation Step on Sorbent Regenerability Over Two Cycles

Sorbent	Run No.	Saturator Temperature °C	Duration of Oxidation Step (hr)	Wt % Sulfur Remaining Regenerated Sorbent After 2 Cycles
CuO/Fe <sub>x</sub> O <sub>y</sub> 2.7 Fe:Cu zeolite	76	70-73	1	----
	77	88-92	1	0.70
	86	95-100	2	----
	87	87-89	2	0.58
CuO/MnO zeolite	72	86	1	----
	73	85	1	0.90
	82	94	2	----
	83	93	2	0.54
CuO/ZnO G66B	80	83-90	2	----
	81	88-92	2	0.276
	92	88-90	1	----
	93	83-85	2	0.20
CuO/ZnO zeolite	74	58-67	1	----
	75	70-73	1	0.68
	88	89-92	2	----
	89	87-91	2	0.58

The lower residual sulfur loadings obtained in the program, in the 0.2-0.5 wt% range, are similar to the levels obtained on regenerated zinc ferrite used in coal gas desulfurization (4,5). This degree of regenerability is promising and may be improved further by optimization of regeneration conditions, particularly gas compositions, bed temperature and duration of regeneration step.

Over the two desulfurization/regeneration cycles, no physical deterioration of the sorbent was noted. Physical deterioration of a sorbent over two cycles would be most unusual; the sorbents must be tested over tens of cycles to determine their physical stability. However, a significant decrease in the BET surface area

over two cycles was noted for the zeolite supported  $\text{CuO/Fe}_x\text{O}_y$  with a 2.7 Fe:Cu atomic ratio. The single-point BET surface areas of the fresh, sulfided, and regenerated sorbents are shown in Table 9. There was a 92% decrease in area between the fresh and sulfided sorbent, probably due to the very large organic sulfur molecules sorbed on the surface. Following two cycles of desulfurization/regeneration on a different sorbent sample, the surface area of the regenerated sorbent was slightly lower than that of the sulfided sample, despite a decrease in the sulfur content. This failure to recover surface area during regeneration may effect the sorbent activity in subsequent desulfurization runs. This will have to be tested over several cycles.

**TABLE 9**

**2.7 Fe:Cu  $\text{CuO/Fe}_x\text{O}_y$  Surface Area and Sulfur Content in Fresh, Sulfided, and Regenerated States**

	FRESH	SULFIDED	REGENERATED
BET SURFACE AREA ( $\text{m}^2/\text{g}$ )	304.2	24.49	21.75
SULFUR CONTENT (wt%)	--	0.71	0.58

Despite the significant change in surface area between the fresh, sulfided, and regenerated sorbents, no significant differences between these states were noted in Scanning Electron Microscopy (SEM) or X-ray Diffraction (XRD) analyses. Samples of fresh, sulfided, and regenerated G66B, zeolite-supported  $\text{CuO/MnO}$ , and zeolite-supported  $\text{CuO/Fe}_x\text{O}_y$  with a 2.7 Fe:Cu ratio were analyzed by SEM. No major differences in the surface characteristics, including particle size, were noted between the different states at magnifications up to 5000X. Samples of fresh, sulfided, and regenerated G66B and zeolite-supported  $\text{CuO/MnO}$  were also analyzed by XRD in an attempt to determine the chemical states of the metals present. Unfortunately, the metal loadings on the zeolite-supported  $\text{CuO/MnO}$  were too low to be detected by XRD. The same was true of the sulfided states of the G66B; with less than a

0.6 wt% sulfur loading, presumably distributed between CuS and ZnS, the concentration of the sulfides in both the sulfided and regenerated samples was too low to detect. The only difference noted in the G66B diffraction patterns was the oxidation state of Cu; in the fresh sorbent, Cu was present as CuO, while in both the sulfided and regenerated samples, metallic Cu was the only copper phase detected.

The regenerability studies in this program were aimed simply at determining if sulfur could be removed from the sulfided sorbent. No attempts to determine the long-term regenerability of these sorbents were made. It is recognized that much further testing is required to determine the suitability of these sorbents for incorporation in a regenerable system.

### **3.3 Sulfur Concentration in Effluent Diesel**

Although the sulfur loadings were low, the sorbents removed a significant portion of the sulfur from the diesel, especially in the early stages of a run. For a sample of condensed diesel taken at 30-45 min. into a run on zeolite-supported CuO/MnO, the sulfur concentration was 0.052 wt%, representing a reduction of over 60% from the 0.134 wt% sulfur concentration in the feed. For this same run, the sulfur concentration in the diesel collected throughout the 4 hour run, was 0.083 wt%. This indicates that the sorbent activity declines throughout the run and to obtain low sulfur concentrations in the effluent, shorter desulfurization cycle times or a larger sorbent bed should be considered.

The highest sulfur removal obtained for a 4 hour run was just under 50% on the G66B sorbent, as shown in Table 10. However, since diesel samples were analyzed for only a small number of runs, in which only a few of the sorbents were tested, conclusions regarding the best sorbent for producing low effluent sulfur concentrations cannot be made. Also, these concentrations reflect only the sulfur concentration in the condensed liquid; in some runs there was also a significant amount of H<sub>2</sub>S in the non-condensable gases.



TABLE 10

## Sulfur Concentration in Effluent Diesel

Run	Sorbent	Diesel S Conc. (wt%)	% S Removal	Comments
4	G66B	0.11	17.9	
5	G66B	0.078	41.8	
11	G66B	0.069	48.5	run for 2 hr at LHSV = $0.5 \text{ hr}^{-1}$
12	G66B	0.068	49.3	
31	2Cu:Zn zeolite	0.112	16.4	run at 500-630°C
32	CuO/Fe <sub>2</sub> O <sub>3</sub> unsupported	0.112	16.4	
86	2.7Fe:Cu zeolite	0.104	22.4	sample at 20-30 min
87	2.7Fe:Cu zeolite	0.15	----	sample at 1 hr
		0.083	38.1	whole run sample
90	CuO/MnO zeolite	0.052	61.2	sample at 30-45 min

From the effluent diesel sulfur concentrations obtained in this program, it appears unlikely that the very low sulfur levels (<10ppm) required for PAFC operation can be achieved by single-stage desulfurization of unprocessed diesel fuel. However, use of this technology to remove approximately 60% of the sulfur from unprocessed diesel before the reformer, followed by a post-reformer regenerable sorbent bed to remove the remaining H<sub>2</sub>S to <10ppm may be a viable alternative to current PAFC fuel processing technology. Replacing the high-pressure bulky HDS unit with an atmospheric pressure regenerable desulfurizer should reduce the weight of the sulfur removal unit by a minimum of 25%, assuming a one-day duty cycle and sorbent sulfur loadings of 1 wt%. A potential drawback to

this change is reduced reformer efficiency due to higher sulfur levels in the feed. Perhaps the combination of a pre-reformer diesel desulfurizer and a sulfur tolerant reformer, such as the Toyo reformer, would provide a more efficient system. Further studies are required to determine the optimum configuration and the overall efficiency and practicality of this fuel processing train, keeping in mind the expected improvements in desulfurization of unprocessed diesel with optimization of sorbent composition and operating conditions.

### **3.4 Effect of Operating Conditions on Sorbent Sulfur Loadings**

In the early stages of this program, the effects of bed temperature, carrier gas composition, and diesel space velocity on sorbent sulfur loading were briefly investigated. Also examined was the effect of reducing the sorbent prior to the desulfurization run.

#### **3.4.1 Temperature**

Temperature was the most studied parameter. Initial desulfurization runs using the G66B sorbent were conducted at 400°C, 500°C, and 650°C. As shown in Table 11, the average sorbent sulfur loadings at 400°C and 500°C were the same, although there was some variation from run to run. A slight increase in sorbent carbon content between 400°C and 500°C was noted, but not enough data is available to determine if this was a real trend or just normal variation in the data. Increasing the bed temperature to 650°C, however, caused a significant decrease in sulfur loading and an equally significant increase in sorbent carbon content. Physical evidence of sorbent coking was also noted at 650°C. Based on the results of these early runs, 650°C was dropped from further testing because of the poor sulfur loading and undesired coking of the sorbent at this temperature.

**TABLE 11****Effect of Temperature on Sulfur Loading and Carbon Content of the G66B Sorbent**

Temperature (°C)	S Loading (Wt%)	Average S Loading (Wt%)	C Content (Wt%)
400	0.488-0.611	0.55	4.01
500	0.40 -0.613	0.55	5.87-6.11
650	0.251-0.275	0.26	10.3-11.4

The early runs showed inconclusive differences between operation at 400°C and 500°C, a trend which continued in further testing. Six different sorbents were tested at both 400°C and 500°C with all other operating conditions fixed. Variations in the sulfur loadings between the two temperatures were noted for individual sorbents, as shown in Table 12. However, no overall trend existed; three of the sorbents had higher loadings at 400°C while two of the sorbents had higher loadings at 500°C, and the average loading on the G66B was the same at both temperatures. To simplify the testing, 500°C was arbitrarily chosen as the temperature to use in the sorbent selection runs.

**TABLE 12****Average Sorbent Sulfur Loadings at 400°C and 500°C**

Sorbent	400°C	500°C
G66B (CuO/ZnO)	0.55	0.55
CuO/MnO zeolite	1.13	0.96
CuO/ZnO zeolite	0.45	0.27
2.7Fe:Cu zeolite	0.60	0.96
CuO/Fe <sub>x</sub> O <sub>y</sub> Al-4126	0.50	0.81
CuO/Fe <sub>2</sub> O <sub>3</sub> unsupported	0.30	0.12

### 3.4.2 Carrier Gas Composition

The effect of three different carrier gases ( $H_2$ ,  $N_2$ , and approximately 50%  $H_2O$  in  $H_2$ ) on sulfur removal was briefly studied. Table 13 lists the loadings obtained with these carrier gases on the G66B sorbent at both 400°C and 500°C. The sorbent loadings using  $H_2$  and  $H_2/H_2O$  were very similar; in fact at 500°C the loadings were the same. However, with  $N_2$  as the carrier gas, the sorbent sulfur loadings were much lower, and also showed a considerable variation with temperature. No conclusions regarding the effect of temperature can be drawn, however, since only one run at each temperature was conducted. The poor sulfur loading with  $N_2$  may indicate that some hydrocracking or hydrogenation reactions of the diesel are required for efficient removal of the sulfur compounds. Due to the poor performance in these initial runs with  $N_2$ , no further tests with  $N_2$  were conducted. A mixture of  $H_2O/N_2$  is another possible carrier gas; the water vapor would supply  $H_2$  for hydrogenation. This composition however, was not tested. Hydrogen was arbitrarily chosen over  $H_2/H_2O$  as the carrier gas to use in the bulk of the testing.

TABLE 13

Effect of Carrier Gas Composition on  
Sorbent Sulfur Loadings

Carrier Gas	Sulfur Loading (wt%) Temperature	
	400°C	500°C
$H_2$	0.553	0.60
$H_2/H_2O$	0.488	0.60
$N_2$	0.154	0.070

### 3.4.3 Space Velocity

The effect of lowering the diesel space velocity on sulfur removal was also examined. A lower space velocity provides more contact time between the diesel and sorbent, and also provides more time for hydrogenation reactions to occur. A lower space

velocity should increase sulfur removal if the reactions are limited by mass transfer or kinetics. The diesel liquid space velocity (LHSV) used in the bulk of the runs was approximately  $4.3 \text{ hr}^{-1}$ , based on a diesel flow rate of  $0.5 \text{ cc/min}$  through the  $7 \text{ cm}^3$  sorbent bed. The space velocity was decreased to approximately  $0.5 \text{ hr}^{-1}$  by cutting the diesel flow rate to  $0.14 \text{ cc/min}$  and by doubling the height, and thus the volume, of the sorbent bed. For the tests at the lower space velocity the duration of the runs were also cut from 4 hours to 2 hours. This was done to maintain high sorbent activity throughout the run.

Unfortunately, the data for the runs at the  $0.5 \text{ hr}^{-1}$  space velocity was quite scattered, with sulfur loadings on the G66B sorbent varying by an order of magnitude, from  $0.016 \text{ wt\%}$ - $0.103 \text{ wt\%}$ . Some of this variation may have been due to fluctuations in the diesel flow rate caused by operating the metering pump at the very low end of its capacity range; however, this is unlikely to be the sole cause of the variation. The possible fluctuation of the diesel flow rate also makes comparison of the loadings obtained on the two different space velocities difficult, since the loadings at the low space velocity must be adjusted for the lower diesel flow rate, as well as for the amount of sorbent and the duration of the run. Due to the wide range of loadings and the other uncertainties, no useful comparisons of performance between the two space velocities can be made. No tests were conducted at the lower diesel space velocity using the pressurized reactor diesel flow system.

#### 3.4.4 Sorbent Pre-Reduction

One other operating parameter, the use of a sorbent reduction step prior to the desulfurization run, was evaluated. This data was also mixed, but tends to show that reduction of the sorbent prior to desulfurization has little effect on sorbent sulfur loadings. This was expected, because  $\text{H}_2$  will quickly reduce the sorbent during the run.

Initial tests of the pre-reduction step were conducted on the G66B sorbent. Prior to the desulfurization run, the sorbent bed, held at 250°C, was purged overnight with 2% H<sub>2</sub> in N<sub>2</sub>. In later tests, on zeolite-supported CuO/Fe<sub>x</sub>O<sub>y</sub> sorbents, the pre-reduction step was accelerated by running 50% H<sub>2</sub> in N<sub>2</sub> through a 500°C sorbent bed for one hour. No comparisons of the reduction efficiencies of these two methods were made.

The sorbent sulfur loadings for desulfurization runs in which the sorbent was pre-reduced and not pre-reduced are listed in Table 14. There was little difference in the G66B loadings. On the zeolite-supported CuO/Fe<sub>x</sub>O<sub>y</sub>, however, the loading for the pre-reduced run was anomalously low.

TABLE 14

Effect of Pre-Reduction on Sorbent Sulfur Loadings

Sorbent	Sulfur Loading (wt%)	
	Pre-Reduced	Not Pre-Reduced
G66B	0.51	0.58
CuO/Fe <sub>x</sub> O <sub>y</sub> 0.9 Cu:Fe zeolite	0.095	0.51
CuO/Fe <sub>x</sub> O <sub>y</sub> 2.7 Fe:Cu zeolite	1.2	0.96

The opposite effect was noted on the zeolite-supported 2.7 Fe:Cu sorbent, where the sulfur loading for the pre-reduced run was slightly higher than the average sulfur loading for runs in which the sorbent was not pre-reduced. These results tend to indicate that reduction of the sorbent prior to desulfurization is not necessary to achieve high sulfur loadings.

### 3.5 Mechanism of Desulfurization

Insight into the reactions that occur during desulfurization of diesel was obtained by examining chromatograms of diesel leaving the reactor during runs with several sorbents. A Varian 3400 gas chromatograph with a sulfur sensitive flame photometric detector was used to analyze samples of diesel collected in the reactor effluent condenser at various times throughout a run. For a detailed description of the chromatographic method used, see Section 2.3. Since there are more than 20 sulfur containing species in diesel, many of them unknown, no attempts to identify the individual compounds were made. The peaks were designated by retention times, which were quite consistent from sample to sample. A typical diesel chromatogram is shown in Figure 3. To compare chromatograms from different samples of treated diesel, the areas of selected peaks were normalized by dividing the peak area by the average area of the corresponding peaks in the untreated diesel samples. The relative areas were then plotted versus peak retention times, and the plots examined for shifts in relative peak size to give some insight into the reactions occurring during desulfurization.

Figure 4 is a plot of the relative peak areas versus retention times for tests on six different sorbents. The samples were taken approximately 30 minutes into a run, which appears to be the time of peak reactivity. All of the runs used standard operating conditions, including a temperature of 500°C and H<sub>2</sub> as the carrier gas. As shown in this figure, for runs on the zeolite-supported sorbents, particularly the CuO/MnO and 2.7 Fe:Cu, the treated diesel has much larger peaks at low retention times and smaller peaks at higher retention times compared to untreated diesel. For unsupported sorbents, the normalized peak areas were considerably smaller and the largest peaks were at slightly higher retention times than for the zeolite-supported sorbents. Also, at the lowest retention times, the peak areas were smaller than in untreated diesel. The behavior on the unsupported sorbents is shown more clearly in Figure 5.

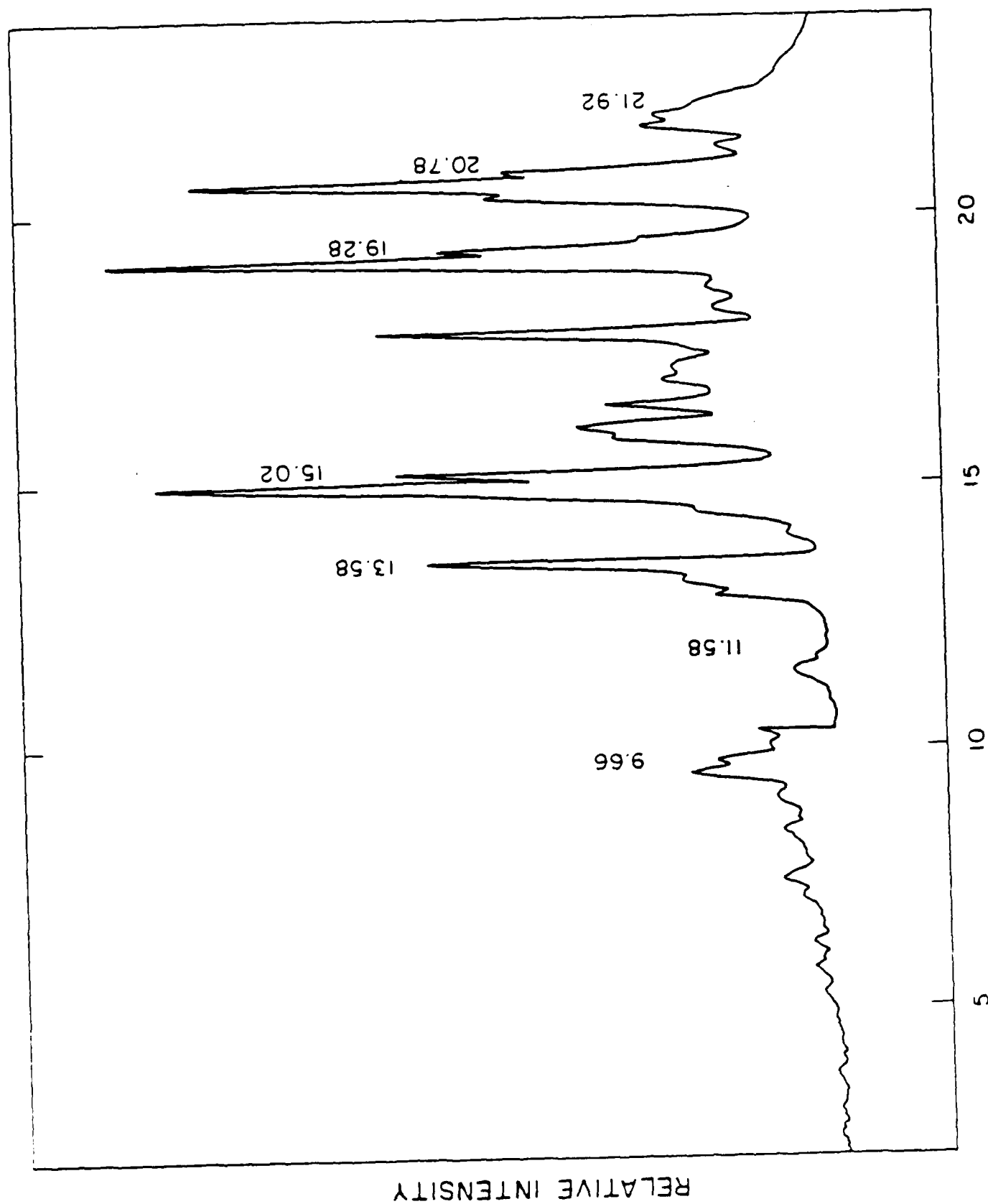


Figure 3. Chromatogram of Unprocessed Diesel



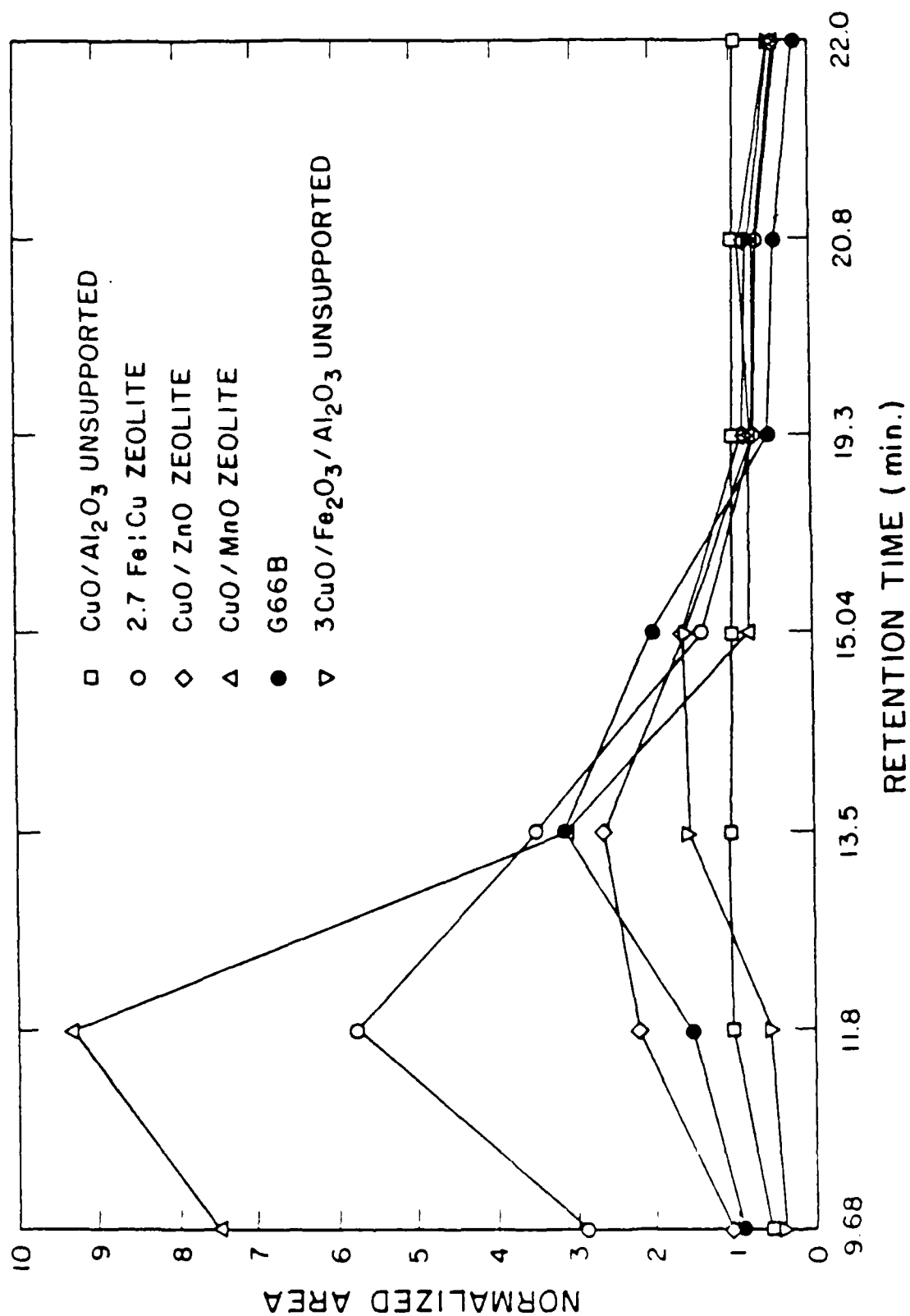


Figure 4. Peak Areas vs. Retention Time for Several Sorbents

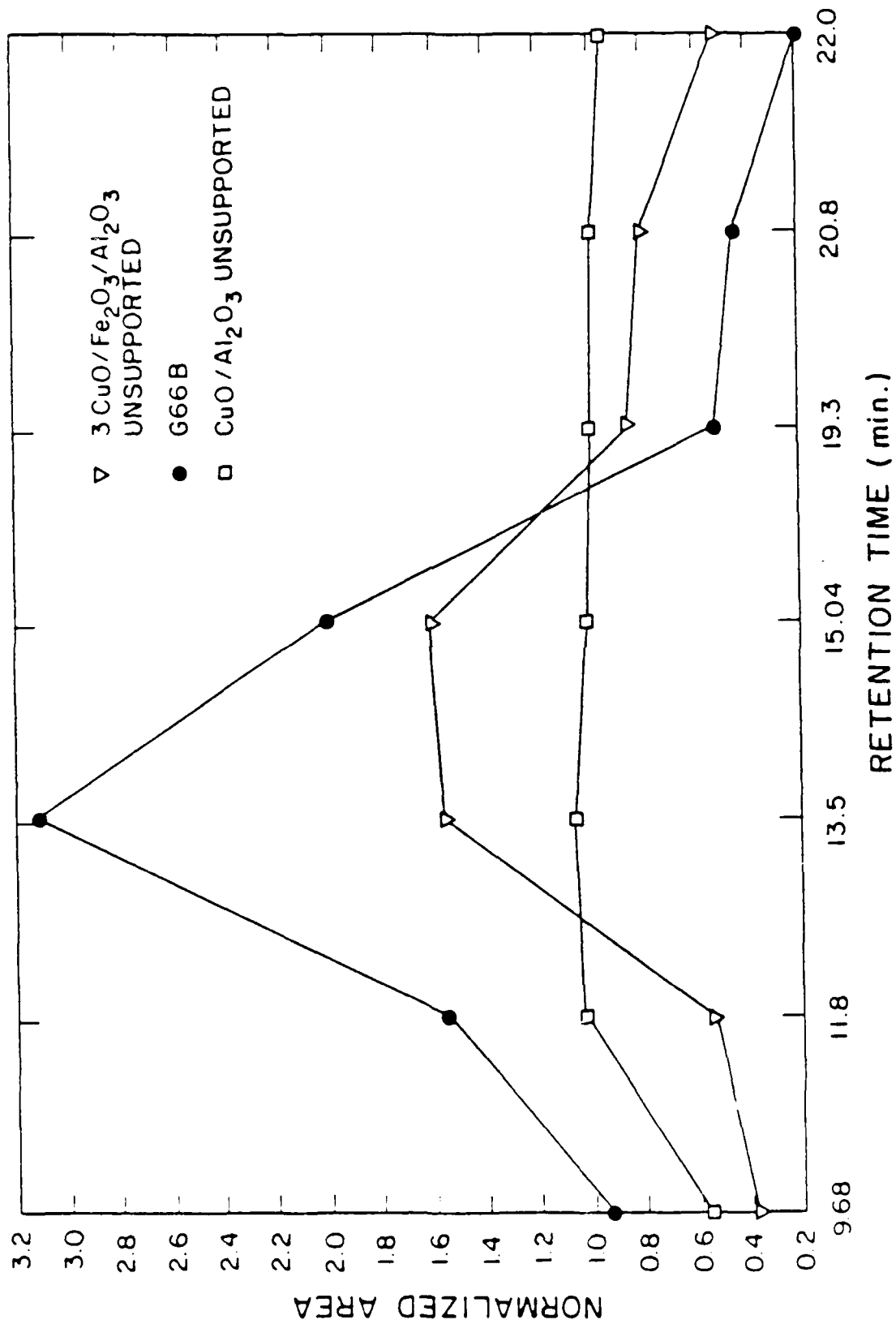


Figure 5. Peak Areas vs. Retention Time for Unsupported Sorbents

These trends in the chromatograms indicate that different reactions may occur on the various sorbents. A possible explanation for the large shift in the relative peak areas from high retention times to low retention times on zeolite-supported sorbents is cracking of the diesel, forming lower molecular weight sulfur species (with lower retention times) from higher molecular weight species. On the unsupported sorbents, however, cracking occurs to a lesser degree, and preferential sorption of the lower molecular weight sulfur species may occur to a greater extent.

The structure of the sorbent, whether supported or unsupported, rather than the type of metal present, appears to influence the degree of cracking. To confirm this, a short run using just the zeolite support was performed. The chromatogram of condensed diesel from this run showed a more pronounced shift to larger peaks at low retention times than occurred during runs on the zeolite-supported sorbents, as shown in Figure 6. Also, very high levels of  $H_2S$  were detected in the reactor effluent during the run on blank zeolite. Thus it appears that the zeolite contributes significantly to cracking of the diesel.

Both diesel cracking and sorption of sulfur compounds appear to be most active in the first hour of a run. This is clearly shown in Figure 7, a typical run-time profile of normalized areas versus retention times for zeolite-supported sorbents. In most cases, the sorbent activity was low during the first ten minutes of a run, but peaked shortly thereafter, at approximately 15-45 minutes into the run, with little change in the chromatograms after one hour. By two hours into the run, the chromatograms were very similar to those of untreated diesel, indicating that the diesel was no longer reacting. It appears that for more efficient sulfur removal, the desulfurization run time should be reduced.

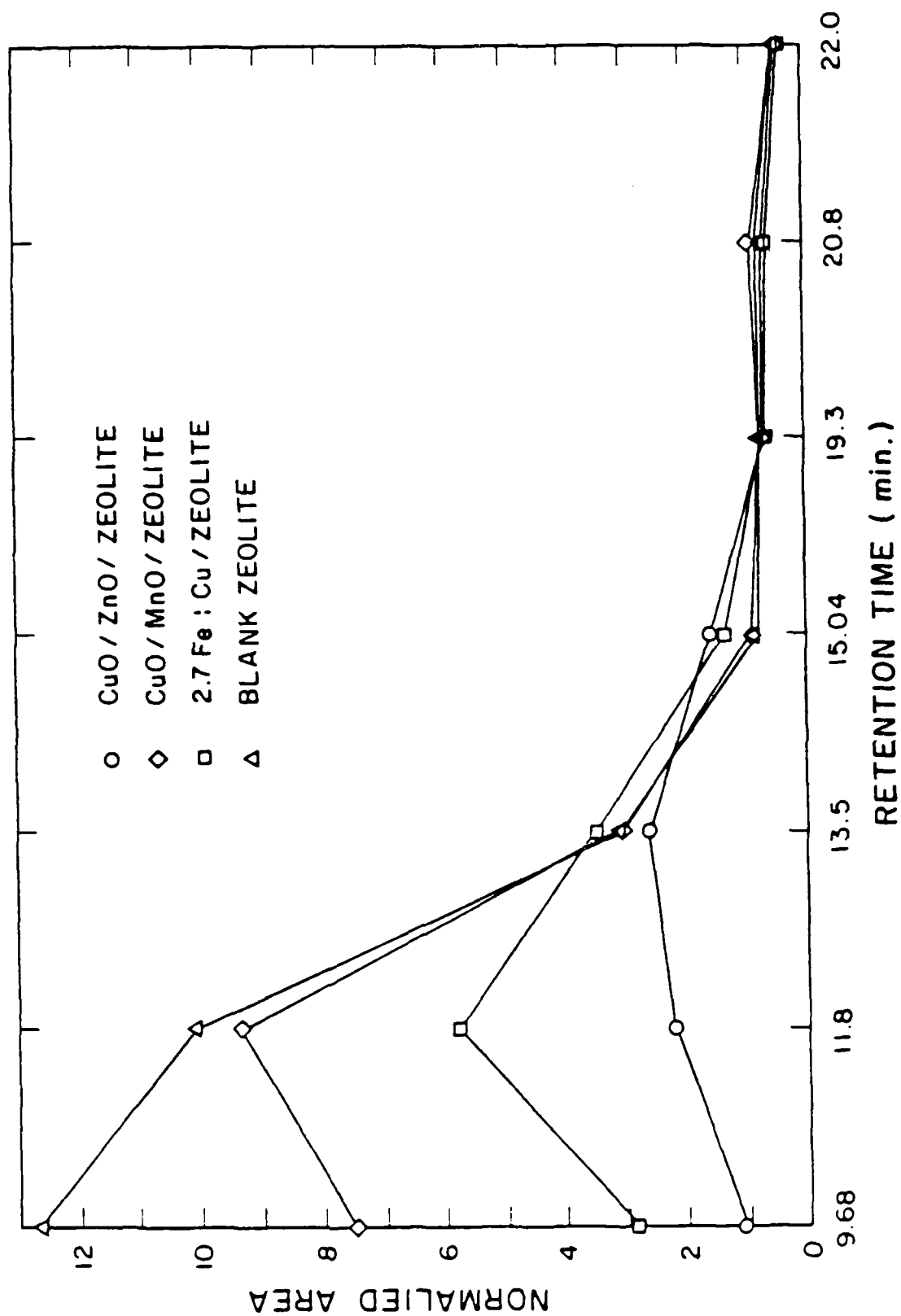


Figure 6. Peak Areas vs. Retention Time for Zeolite-Supported Sorbents

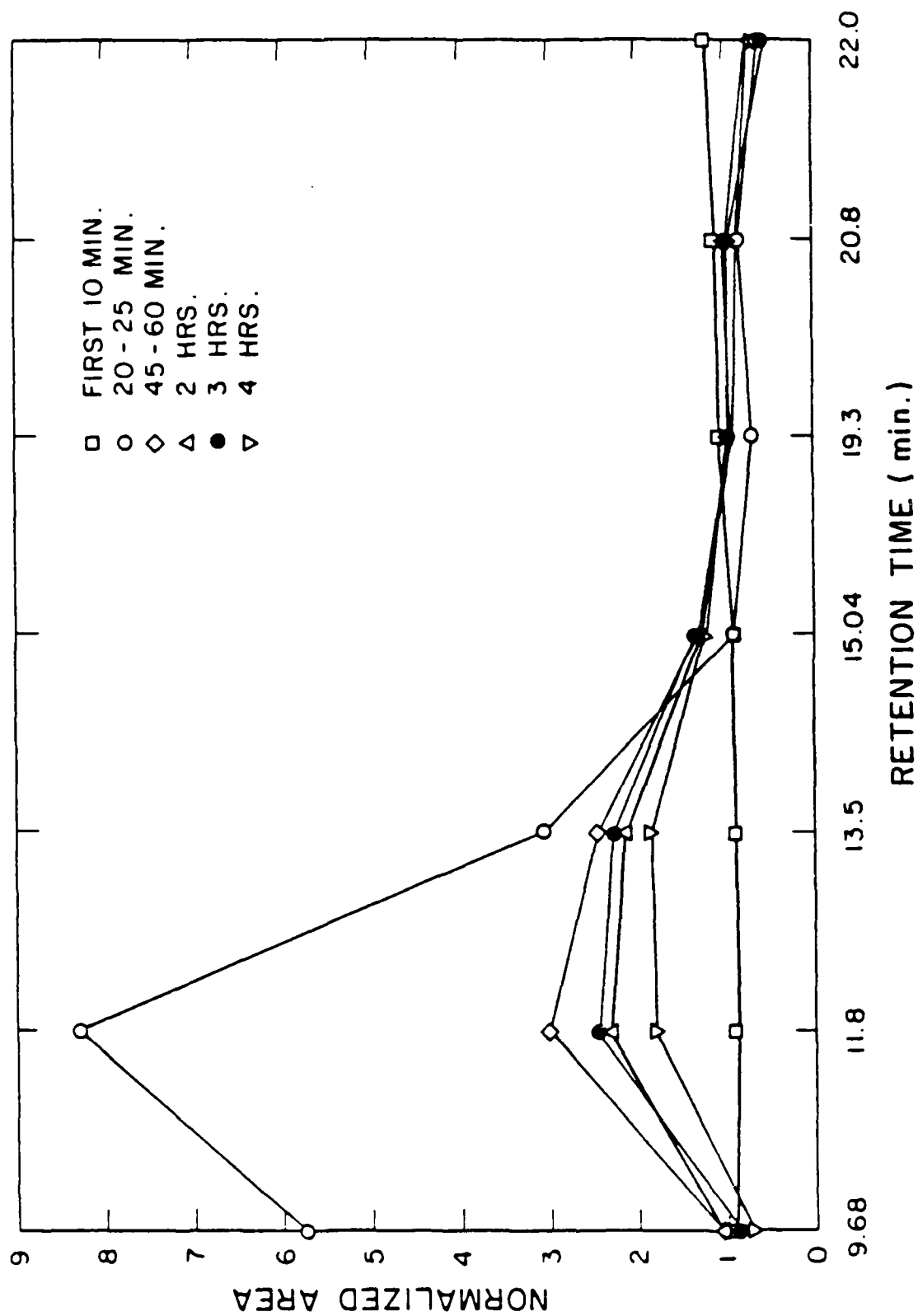


Figure 7. Peak Areas vs. Retention Time at Various Times During a Desulfurization Run

## 4.0 CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

### 4.1 Conclusions

Technology for the direct desulfurization of unprocessed diesel fuel using regenerable mixed metal oxide sorbents was developed. Removal of greater than 60% of the sulfur in diesel fuel was demonstrated, and sorbent sulfur loadings of approximately 1 wt% were attained. Preliminary studies indicated that the sorbents are regenerable, with up to 70% of the sorbed sulfur removed during regeneration.

Of the fourteen sorbents tested, the three best appear to be: zeolite-supported  $\text{CuO/Fe}_x\text{O}_y$  with a 2.7 Fe:Cu atomic ratio; zeolite-supported  $\text{CuO/MnO}$ ; and alumina-supported  $\text{CuO/Fe}_x\text{O}_y$ . These sorbents had the highest sulfur loadings, and also exhibited good regenerability. The conversion of the metal oxides to sulfides on the supported sorbents was approximately 20%, considerably higher than the conversions attained on the unsupported sorbents.

The mechanism of direct desulfurization of diesel is complex and is not completely understood, but partial cracking of the diesel occurs, as well as direct sorption of some of the large organic sulfur compounds. Cracking of the diesel is more severe on zeolite-supported sorbents than on other sorbents tested.

Incorporation of the technology for desulfurization of unprocessed diesel fuel into a PAFC power plant may decrease the size and weight of the fuel processing system. An alternative to current PAFC fuel processing technology may be a pre-reformer sorbent bed, using the technology for desulfurization of unprocessed diesel, followed by a post-reformer regenerable sorbent bed to remove the remaining  $\text{H}_2\text{S}$ . Replacing the high pressure bulky HDS unit with an atmospheric pressure desulfurizer should reduce the weight of the sulfur removal unit by a minimum of 25%, assuming a one-day duty cycle and sorbent sulfur loadings of 1 wt%.

Improvements in sorbent sulfur loading, sulfur removal efficiency and sorbent regenerability are expected with optimization of sorbent composition, sorbent structure, and operating conditions. With improvements in sorbent sulfur loadings, further reductions in size and weight of the fuel processing unit are expected; increasing the sorbent sulfur loading to 5 wt% would reduce the weight of the sulfur removal unit by a minimum of 75%, assuming a one-day duty cycle.

#### **4.2 Future Work**

Future research on sorbent optimization should investigate possible modifications to both the sorbent composition and structure. In addition to copper, iron, and manganese oxides, the substitution or addition of other select metal oxides should be evaluated. Further studies are also required to determine the optimum ratio of the oxides and, for supported sorbents, the optimum metal loading. Regarding sorbent structure, further studies of support material, with emphasis on minimizing the extent of cracking of the fuel, are recommended. Included in these studies should be zeolites and aluminas with neutral or basic compositions.

In addition to optimization of sorbent composition and structure, further research on the long-term regenerability of these sorbents, including expected sorbent life, structural stability, and optimization of regeneration conditions, should be conducted. Other potential areas for future research are optimization of process operating conditions and reactor dimensions, detailed studies of the mechanism of desulfurization, and extension of this technology to desulfurization of other liquid fuels. Systems and cost analyses, including tradeoff studies of efficiency versus cost, should also be conducted.

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